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Quality characteristics of effluent receiving waters of Benin River adjacent to a lubricating oil producing factory, Nigeria

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Abstract

Untreated (or partially treated) effluents are capable of polluting a receiving water body. An environmental audit of the Benin river adjacent to a lubricating oil producing factory was carried out. Dry and rainy seasons effluent and water samples were collected for two years (water samples from seven sampling stations i.e. two upstream and five downstream). Physicochemical variables (including oil variables) were analyzed by standard methods and toxic metals by flame atomic absorption spectrometry. Important results include Oil and Grease (2270±480 μgl^{-1}), total petroleum hydrocarbon (2010±340 μgl^{-1}), Pb (146±55 μgl^{-1}), Ni (1880±630 μgl^{-1}) and pH (6.02±0.09). Some of these variables and metals exceeded guidelines values for drinking water quality. Water is polluted and needs to be rigorously treated before use for drinking purpose.

Keywords:*Benin river, lubricating oil producing factory, physico chemical variables, toxic metals, oil and grease, total petroleum hydrocarbon, drinking water quality, flame atomic absorption spectrometry*

Introduction

Important sources of petroleum hydrocarbons and heavy metals in the environment include petroleum prospecting and processing industry, petroleum refining and petrochemical industries, and wastes from auto- mobile mechanic workshops (waste containing used and unused lubricating oils) (Forstner and Whittman, 1983; GESAMP, 1993). The Niger Delta environment is known to have received high concentrations of petroleum hydrocarbons from the upstream sector of the petroleum industry through the instrumentation of oil spillages (Horsefall and Spiff, 2002; UNDP, 2006). It has been estimated that three million barrels of crude oil have been spilled into the Niger delta environment in 6817 separate spills between 1976 and 2001 (UNDP, 2006). The effect of the presence of high concentrations of petroleum hydrocarbons can be severe; they include damage to and loss of biodiversity, depletion of arable land, depletion of available potable water and blockage of water ways (Nwilo and Badejo, 2007; NRC, 2003; Luiselli *et al*., 2004; Luiselli *et al*., 2006; Odokuma and Okpokwasili, 2004; Omo-Irabor *et al*., 2011). Reported studies of effects of the petroleum industry (both upstream and downstream sectors) on the environment of the Niger Delta have revealed that high concentrations of total petroleum hydrocarbon (TPH), polynuclear aromatic hydrocarbons and trace heavy metals are present in waters, sediments and soils of the Niger Delta (Ekpo et al., 2012; Onianwa et al.,2001; Iwegbue et al., 2008; Nduka and Orisakwe, 2011; Davies and Abowei, 2009; Akporido and Imah, 2009; Otukunefor and Obiekwu, 2005; UNEP, 2011).The physicochemical characteristics of a refinery effluent and the physicochemical characteristic of water and sediment of an effluent receiving water body was investigated (Otukunefor and Obiekwu, 2005). They observed that treated refinery effluent contained very high concentrations of phenol (11.06 mg/L), oil and grease (7.52 mg/L), ammonia (8.52 mg/L), COD (91.76 mg/L), TDS (390.6 mg/L) and phosphate (6.2 mg/L), but low concentrations of sulphide, nickel, lead, copper and chromium which were undetected. They also observed high concentrations of phenol (5.13 – 16.38 mg/L), oil and grease (10.56 – 15.23 mg/L) and ammonia (4.31 – 13.17 mg/l) in the receiving water. The Benin river takes it source from an area

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about 150 km northeast of Koko town and flows through Koko ton and its adjoining area into the Bight of Benin. The river serves the people of the area for dinking purpose, for fishing and for transport. The adjoining land is used for farming. Farm products obtained from the area include: vegetables, palm oil, cassava and yam. There has not been any reported incident of crude oil spillage in the vicinity of Koko town. There has however been the incident of the deposition of hazardous waste originating from Italy in a part of Koko town which attracted the attention of the Federal Government of Nigeria and the international community (Kocasoy, 2003). A large proportion of the waste was finally evacuated and re-exported to Italy (Kocasoy, 2003). Most the reported works on the Niger delta environment have so far been focused on the effect of petroleum prospecting and processing industry as already indicated. Some work has also been carried out on the effect of effluents from refineries and petroleum product depots (UNEP, 2011; Otukunefor and Obiekwu, 2005) and on auto-mobile mechanic waste dumps (Iwegbue et al., 2008; Akporido and Imah, 2009). In one of these studies elevated concentrations of TPH was observed in which the source was inferred to be from the deliberate or in deliberate spilling of used and unused lubricating oil on the soil (Iwegbue *et al*. 2008). No work has however been reported on the effect of effluents from a lubricating oil producing factory on the water, sediment and soil of an area close to such a factory. The hypothesis of this study is to assess the effect of effluents from a lubricating oil producing factory on the physicochemical parameters, the toxic metal contents and the oil contents (total organic extracts and total petroleum hydrocarbons) in waters of Benin River adjacent to the factory it is expected that, effluents from such a factory should affect these parameters in water of such an environment. There is also a dearth of information on the effect of effluents from lubricating oil producing factories in the Niger Delta region. The present study examined the effect of effluents from a lubricating oil producing factory on the waters of a river which receives such effluents by determining some physicochemical variables, total petroleum hydrocarbons (TPH) total organic extracts (TOE), and selected toxic metals of both the effluents and waters of the receiving river.

Material and methods

The study area is shown in Figure 1 (Map of study area showing a section of Benin River and the location of the lubricating oil factory) Water samples were collected from seven sampling stations. Two of the sampling stations are located upstream from the point of entry of effluents into the river. One sampling station is at the point of entry of effluents into the river and four others sampling stations are located downstream from this point successively. The two upstream stations are at Ubakporo (UBAK) and at Arunologbo (ARUN). The sampling station at the point of entry of effluent is designated as Point of Entry of effluents (PEE). The other four sampling stations are at Ajalugbeti (AJA), this is followed by Uba-Iro (UBA), Uba-Tailor (UB-TA) and at Ilogun (ILOG). The Benin River flows from Ethiope West Local Government of delta State in the direction southwest into the Bight of Benin in the Atlantic Ocean. It flows past Koko town in which is situated the lubricating oil producing factory. Fig. 1 is map of study area showing a section of Benin River and location of Lubricating oil producing factory in Koko town. Water samples were collected twice every season (i.e. once in each quarter of the year). Samples were collected in dry and rainy seasons for two years. Effluent samples were also collected each time water samples were collected from the river. Effluent samples were collected from the conduit pipe where it discharges effluents into the river.

Samples were taken for the following parameters: pH, temperature, total suspended solids (TSS), total dissolved solid (TDS), dissolved oxygen (DO) biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), oil and grease (O&G), and total petroleum hydrocarbon (TPH) and the heavy metals (Ni, Cd, Pb, Cr, and Zn).

The period of sampling was from June 2007 to March 2009. Grab samples of water were collected manually from near the middle axis of the river at the surface (1 m to the surface) and at mid-depth by covering the mouth of the sample bottle and opening it at the desired depth to collect the water samples.

The bottle lid is now replaced before withdrawing the sampling bottle from the water. The effluent samples were collected by compositing grab

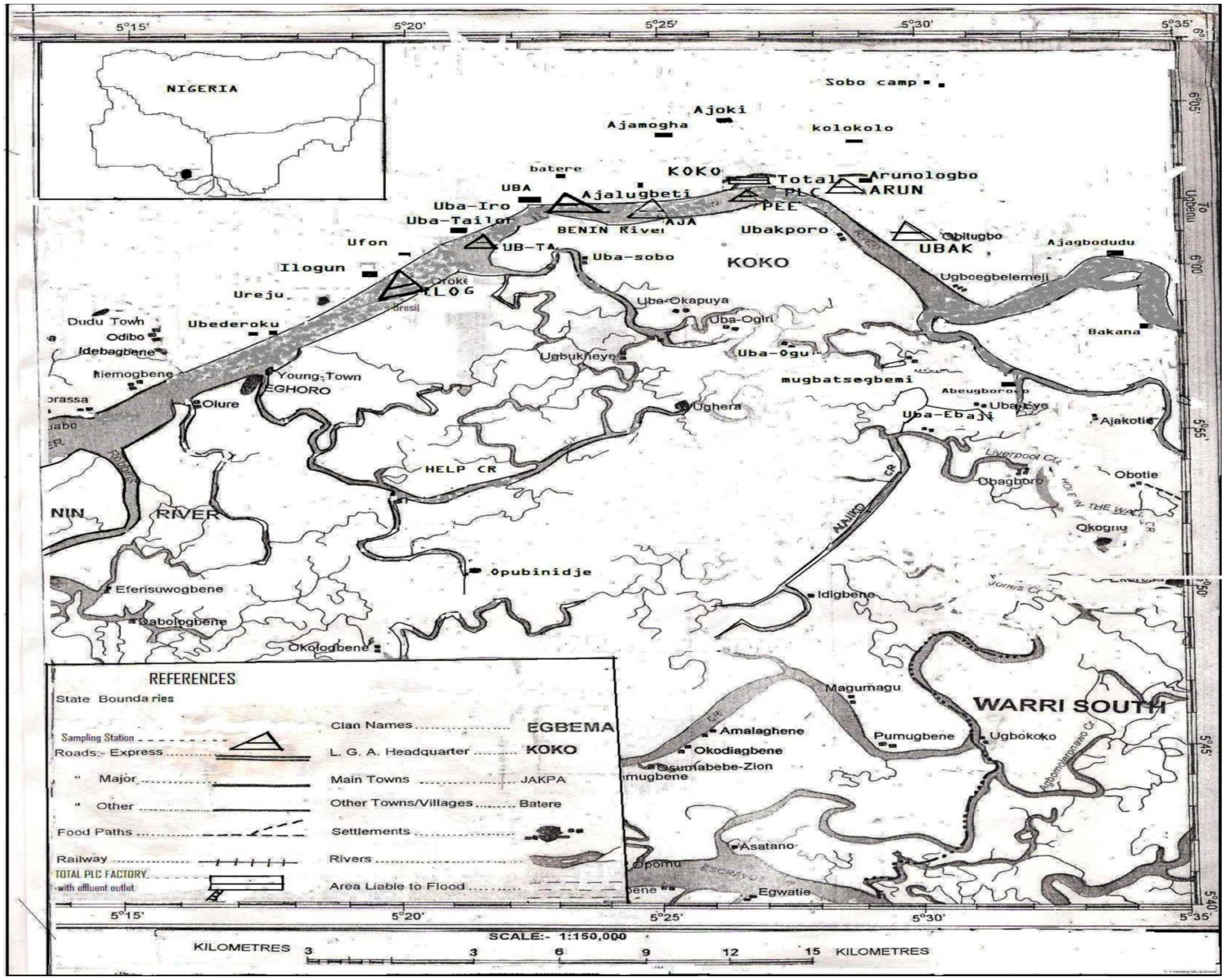

Figure 1: Map of study area showing a section of Benin River and the location of the lubricating oil factory
Source: Directorate of Land and Survey Governor's Office, Asaba, Delta State, Nigeria

samples collected every 20 mins for 2 hrs. Water and effluent samples were preserved for each parameter as described in standard methods (APHA-AWWA-WEF, 1995). The temperature of samples was determined at the site with mercury bulb thermometers.The pH of water samples was determined by a portable pH- meter (pH-meter model test WP) at the site. The determination of TSS was carried out by filtering water sample using gooch crucible -suction pump system and drying the filtered solid in an oven at 103^0C to constant weight (APHA-AWWA-WEF, 1995). The TDS was determined by evaporating the filtrate (in the TSS determination) in an evaporating dish in a steam bath and drying the residue in an evaporating dish in an oven at 180 ^{0}C to constant weight (APHA-AWWA-WEF, 1995). DO was determined by the iodometric method (azide modification) as described in standard method (APHA-AWWA-WEF, 1995). The 5-days BOD test was employed in the determination of BOD_5 of water samples (APHA-AWWA-WEF, 1995). The open reflux method was used in the determination of COD of samples (APHA-AWWA-WEF, 1995). The O&G of samples was determined by partition-infrared method with oil obtained from the lubricating oil factory acting as reference oil and as in standard method (5520C) (APHA-AWWA-WEF, 1995). The TPH of water samples was determined from the hexane extract used for the oil and grease measurement by first carrying out a clean up procedure on the extract by the addition of 4g. of activated silica gel with stirring using a magnetic stirrer for 5 min. and measuring TPH by partition-infrared (method 5520F) (APHA-AWWA-WEF, 1995).Water samples were pre-concentrated by evaporation simultaneously with digestion by addition of 5ml Concentrated. HNO_3. Toxic metals (Ni, Cd, Pb, Cu and Zn) were determined from the digest solution by flame AAS. Details of experimentation are as stated in standard methods (APHA-AWWA-WEF, 1995). A quality assurance programme was put in place in the study and it involved determination of blanks and duplicates, determination of glucose-glutamic acid check for BOD_5 determinations, determination of % recovery for COD by determining COD on standard solutions of potassium hydrogen phthalate (KHP) (i.e. solution which contains 425 mg/L of KHP) and comparing the mean of five determinations to the theoretical value of 500 mgl^{-1} (APHA-AWWA-WEF, 1995). The percentage recoveries of O&G, TPH and the five toxic metals were also determined. The following average percentage recoveries were obtained for five determination of each parameter: COD (93.2 ± 4.7%), O&G (93.6 ±8.4), TPH (95.2 ±7.7%), Ni (91.4 ±6.3%), Cd (92.7 ±9.1%), Pb (99 ±5.8%), Cr (98.3 ± 7.5%) and Zn (101 ± 8.7%). These percentage recoveries all falls within the range 90 – 110 which means good percentage recoveries were obtained for all the parameters. Using Microsoft Excel (Microsoft Corporation LTD), ANOVA-single factor analysis was used for the comparison of means of each of the variables in the four seasons studied (two dry and two rainy seasons) and the mean of each variable in five sampling stations in the study area, and the t-test (two sample, assuming equal variance) was used to compare the means of some of the variables of the study area with those of the control area. The Pearson 2-tailed test was used for the correlation of the values of all variables (with the exception of the pH values) within the Statistic Package for the Social Sciences (SPSS) (version 17) (SPSS, Chicago).

Results and Discussion

The results obtained shows that the average concentrations of the two oil parameters in the study area i.e. O & G (2270±480 μg/L and TPH (2010±340 μg/L) are high as expected. Other results which also indicated that the quality of water in the study area is low are the average values of Ni (1880±630 μg/L), Pb (146±55 μg/L), Zn (62±42 μg/L), Cd (3.0±5.3 μg/L), COD (80±38 μg/L) and DO (2.96±0.90 μg/L). A definite pattern in the variation of the values of measured parameters with distance from point of discharge of effluents to downstream to the furthest sampling station (i.e. ILOGUN) was not observed (Table 2). The differences in the values of the measured parameters with sampling stations were only statistically significant for COD and Cd using ANOVA- single factor analysis.. Also none of the values of measured parameters are highest at point of discharge of effluent as might be expected. The values of most parameters were higher in the study area (downstream) sampling stations than in the control area sampling stations (Tables 1 & 3).

Cd was not detected in any of the control sampling stations but significant amount was observed in each of the study area sampling stations. Also a comparison of the values of some of the measured variables within the study area with those within the control area using t-test (two sample, assuming equal variance) shows that the differences were statistically significant for COD, O & G, TPH, Ni, Pb, and Zn. The differences in the concentrations of O & G and TPH between the study area and the control area indicates that a significant amount of oil related substances entered the river at the point of discharge of effluents into the river (PEE). A comparison of the values of the physicochemical characteristics in the different seasons shows that there are no statistically significant changes in the physicochemical characteristics of study area water with seasons (ANOVA-Single factor) (Table 2). The concentrations of Ni (1970±670 μgl^{-1}), O&G (2340±480 μgl^{-1}) and TPH (2040±350 μgl^{-1}) were however much higher in the second dry season. The concentration of Zn (67±48 μgl^{-1}) and Pb (154±59 μgl^{-1}) were higher in the second rainy seasons than the concentrations for the two parameters in the other three seasons.Also, a comparison of concentrations of heavy metals in effluents with two national effluent limitation guidelines (Nigeria) i.e. effluent limitation guidelines of the Federal environmental protection agency (FEPA) (now Federal ministry of environment (FMEnv)) (FEPA, 1991) and that of the Department of Petroleum Resources (DPR) (DPR, 2002) shows the

Table 1: Average values of Physico chemical characteristics of each Sampling Station

Parameters	Upstream(control) sampling Stations		Downstream (Study area) Sampling Stations				
	UBAK	ARUN	PEE	AJA	UBA	UB-TA	ILOG
Temp. ^{0}C	32.1±1.0	32.4±0.9	30.9 ± 0.6	30.5 ± 0.8	30.4 ± 1.1	30.8 ± 1.3	31.8 ± 0.7
pH at 25^{0}C	6.08±0.04	6.05±0.06	6.0 ± 0.04	5.96 ± 0.11	6.02 ± 0.09	6.07 ± 0.04	6.06 ± 0.10
TSS (mgl^{-1})	6.1±1.1	7.6±1.5	67 ± 1.6	6.2 ± 1.1	6.1 ± 1.4	6.5 ± 1.4	7.5 ± 2.7
TDS (mgl^{-1})	19.8±1.6	22.1±1.7	18.6 ± 4.4	21.1 ± 6.3	24.0 ± 6.1	19.8 ± 2.8	28.5 ± 3.9
DO (mgl^{-1})	4.36±0.68	4.24±0.32	3.7 ± 1.3	2.56 ± 0.51	3.25 ± 0.56	2.12 ± 0.19	3.18 ± 0.59
BOD$_5$ (mgl^{-1})	7.48±0.91	5.20±0.96	7.7 ± 2.3	5.3 ± 2.0	6.1 ± 2.6	4.6 ± 2.4	8.34 ± 0.64
COD (mgl^{-1})	65±12	13.4±4.9	114 ± 11	120 ± 5.8	78 ± 19	68 ± 13	21.7 ± 5.3
O & G (µgl-1)	1810±300	2060±250	1960 ± 230	2380 ± 330	2300 ± 640	2260 ± 460	2470 ± 590
TPH (µgl^{-1})	1540±80	2000±250	1740 ± 140	2170 ± 250	2010 ± 520	2160 ± 310	1980 ± 240
Ni (µgl^{-1})	940±580	1390±1100	1730 ± 690	1660 ± 250	1630 ± 240	1630 ± 570	2740 ± 500
Cd (µgl^{-1})	ND	ND	2.4 ± 1.8	9.6 ± 9.1	1.5 ± 3.5	2.4 ± 1.4	0.38 ± 0.52
Pb (µgl^{-1})	107±110	63±64	154 ± 36	134 ± 94	134 ± 54	147 ± 49	163 ± 20
Cr (µgl^{-1})	0.38±0.52	1.00±0.93	0.50 ± 0.53	0.50 ± 0.76	0.25 ± 0.46	0.50 ± 0.76	0.25 ± 0.46
Zn (µgl^{-1})	22.8±3.1	20.6±3.9	58 ± 15	61.4 ± 9.9	56 ± 50	32 ± 19	103 ± 61

Table 2: Average Values of Physicochemical Parameter in each Season

Parameters	**First Dry Season**	**First Rainy Season**	**Second Dry Season**	**Second Rainy Season**
Temperature ^{0}C	30.6 ± 0.8	30.9 ± 0.7	31.3 ± 1.3	30.7 ± 1.1
pH	6.04 ± 0.03	6.01 ± 0.10	6.04 ± 0.05	6.01 ± 0.15
TSS (mgl^{-1})	5.6 ± 1.2	6.8 ± 1.5	6.7 ± 2.1	7.3 ± 1.8
TDS (mgl^{-1})	23.0 ± 5.8	22.0 ± 5.5	22.0 ± 6.2	22.7 ± 6.7
DO (mgl^{-1})	2.58 ± 0.74	3.10 ± 0.82	3.0 ± 1.1	3.21 ± 0.88
BOD$_5$ (mgl^{-1})	5.6 ± 2.5	6.3 ± 2.7	7.0 ± 2.0	6.7 ± 2.7
COD (mgl^{-1})	79 ± 41	82 ± 40	79 ± 37	81 ± 39
O & G (µgl^{-1})	2260 ± 440	2260 ± 500	2340 ± 480	2230 ± 580
TPH (µgl^{-1})	1990 ± 270	2000 ± 350	2040 ± 350	2030 ± 430
Ni (µgl^{-1})	1880 ± 630	1820 ± 680	1970 ± 670	1830 ± 640
Cd (µgl^{-1})	2.6 ± 6.9	3.4 ± 4.1	3.0 ± 4.4	3.0 ± 6.1
Pb (µgl^{-1})	142 ± 53	148 ± 57	141 ± 58	154 ± 59
Cr (µgl^{-1})	0.00	0.60 ± 0.70	0.50 ± 0.71	0.50 ± 0.53
Zn (µgl^{-1})	58 ± 41	62 ± 41	62 ± 43	67 ± 48

following: the average concentration of Zn in effluent (5140±710 µgl^{-1}) exceeded both the FEPA guideline (5000 µgl^{-1}) and the DPR guideline value (1500 µgl^{-1}), The average concentration of Pb in effluent (2380±210 µgl^{-1}) exceeded both the FEPA (50.0 µgl^{-1}) and the DPR (50.0 µgl^{-1}) effluent guideline values, while the average concentration of Cr in effluent (35.0±5.5 µgl^{-1}) exceeded only the DPR effluent guideline Value (30.0 µg/l^{-1}). These results indicate that the effluents from the lubricating oil producing factory are polluted and have capability to pollute a receiving water body. A very important observation however is that the average concentration of Ni in effluent (10.2±5.2 µgl^{-1}) exceeded the guideline value for FEPA (10.0 µgl^{-1}) slightly (DPR have no value for Ni) and is

Table 3: Average values of Physico chemical characteristics and heavy metals in study and control areas

Parameters	Study Area	Control Area
Temperature ^{0}C	30.9 ± 1.0	32.0 ± 0.9
pH at 25^{0}C	6.02 ± 0.09	6.06 ± 0.05
TSS (mgl^{-1})	6.6 ± 1.7	6.9 ± 1.5
TDS (mgl^{-1})	22.4 ± 5.8	21.0 ± 2.0
DO (mgl^{-1})	2.96 ± 0.90	4.30 ± 0.51
BOD_5 (mgl^{-1})	6.4 ± 2.5	6.3 ± 1.5
COD (mgl^{-1})	80 ± 38	39 ± 28
O & G (µgl^{-1})	2270 ± 480	1930 ± 300
TPH (µgl^{-1})	2010 ± 340	1770 ± 300
Ni (µgl^{-1})	1880 ± 630	1170 ± 890
Cd (µgl^{-1})	3.0 ± 5.3	0.00
Pb (µgl^{-1})	146 ± 55	85 ± 89
Cr (µgl^{-1})	0.40 ± 0.59	0.69 ± 0.79
Zn (µgl^{-1})	62 ± 42	21.7 ± 3.6

also much less than the average concentration obtained in the river water (1880±630 µgl^{-1}). This invariably means that the high average concentration of Ni in the river water does not come from the effluent of the factory. It is suspected that nickel containing materials must have entered the river some where upstream. High concentration of Ni was also observed in the waters of the two upstream sampling stations. A comparison of values of physico chemical characteristics and toxic metals obtained in this study with several guideline values (Table 3) gives the following: The average pH value (6.02 ± 0.09) falls below the range for maximum acceptable levels of the Canadian Drinking Water Standards (6.5 – 8.5) maximum admissible concentration (MAC) of EEC Drinking Water Standards (6.5 – 8.5) (Sayre, 1988), Permissible Limit (PL) of FEPA (6.5 – 8.5), Nigeria Water Quality: Drinking water standards (FEPA,1991) and the secondary maximum contaminant level (SMCL) of U.S.A. Secondary Drinking water Standards (This is non-enforceable) (USEPA, 2004). All these indicate that the water is slightly too acidic to serve as drinking water. The O & G value (2270 ± 480µgl^{-1}) and TPH value (2010 ± 340 µgl^{-1}) exceeds the permissible limit of FEPA, Nigeria water quality: drinking water Standards (50.0 µg/L) (FEPA, 1991) which shows there is too much oil related substance in the water of the study area. The average concentration of Ni of the study area (1880 ± 630 µgl^{-1}) by far exceed the WHO's 2006 drinking water standards (70.0 µgl^{-1}) and the permissible limit of FEPA Drinking water standards (50.0 µgl^{-1}). The average value of Pb in the study area (146 ± 55 µgl^{-1}) far exceeds all the guideline values (Table 3), these shows that water of the area is polluted for purpose of drinking and not fit to serve as drinking water. A comparison of the average values of the physicochemical variables and toxic metals of the water of the study area with some guidelines for non-drinking uses of water (Table 6) shows that: the average pH of water (6.02 ± 0.09) falls below the pH range for the following guidelines values: fine paper production of the pulp and paper industry (6.8 – 7.0) of the Canadian water quality guideline (WQGs) (Canadian council of Resource and Environment Ministers (CCREM), 1987), Boiler feed water of power generating industry (8.8 – 9.4) of the Canadian WQGs (CCREM, 1987), food canning and freezing dried processes of the Beverage industry (6.5 – 8.5) of the Canadian WQGs (CCREM,1987), limiting concentration of irrigation water (7.0 – 8.5) of the Food and Agricultural Organization (FAO) Aquatic life protection water (freshwater) of the California State Water Quality Control Board (CSWQCB) (6.5–8.5) and dyeing process of the Textile industry (7.5–10.0) of the Federal Environmental Protection Agency (now Federal Ministry of environment).

Table 4: Comparison of average concentration of heavy metals in effluent with FEPA and DPR effluent limitation guideline values

Heavy metals	Concentrations of Heavy metals	FEPA Interim Effluent Limitation Guidelines (FEPA, 1991).	DPR Effluents Limitation Guidelines (DPR, 2000)	Inferences
Ni (μgl^{-1})	<5.00	10.00	No guidelines	Did not exceed any of the guidelines
Cd (μgl^{-1})	<5.00	10.00	No guidelines	Did not exceed any of the guidelines
Zn (μgl^{-1})	5140 ± 720	5000	1,500	Exceeded both guidelines
Pb (μgl^{-1})	2380 ± 210	50.0	50.0	Exceeded both guidelines
Cr (μgl^{-1})	35.0 ± 5.5	50.0	30.0	Exceeded DPR guidelines

FEPA = Federal Environment Protection Agency (now Federal Ministry of Environment, Nigeria)
DPR = Department of Petroleum Resources (Nigeria)

Table 5: Average Values (Concentrations) of Physicochemical Characteristics and heavy metals of study area compared with some National and International Drinking Water Standards

Parameters	Results from present study of Benin River	Max. Permissible Level of the National Drinking Water Standards, Nigeria (SON, 2007)	Health based guideline of WHO's Drinking Water Standards, 2006 (WHO, 2006)	Max. Contaminant level of USA Drinking Water Standard (USEPA, 2004)	Max. Acceptable level of Canadian Drinking Water Standards (CCREM, 1987)	Max. Admissible Concentration of EEC Drinking Water Standards (Sayre, 1988)	Permissible Limit of FEPA, Nigeria Water Quality: Drinking Water (FEPA, 1991)
Temp. ^{0}C	30.9 ± 1.0	Ambient					
pH at 25^{0}C	6.02 ± 0.09	No guideline	No guideline	6.5 – 8.5*	6.5 – 8.5	6.5 – 8.5	6.5 – 8.5
TSS (mgl^{-1})	6.6 ± 1.7	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline
TDS (mgl^{-1})	22.4 ± 5.8	No guideline	No guideline	500*	No guideline	No guideline	No guideline
DO (mgl^{-1})	2.96 ± 0.90	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline
BOD_5 (mgl^{-1})	6.4 ± 2.5	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline
COD (mgl^{-1})	80 ± 38	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline
O & G (μgl^{-1}	2270 ± 480	No guideline	No guideline	No guideline	No guideline	No guideline	50.0*
TPH (μgl^{-1})	2010 ± 340	No guideline	No guideline	No guideline	No guideline	No guideline	50.0
Ni (μgl^{-1})	1880 ± 630	No guideline	70.0	No guideline	No guideline	No guideline	50.0
Cd (μgl^{-1})	3.0 ± 5.3	3.00	3.00	5.00	5.00	5.00	10.00
Pb (μgl^{-1})	146 ± 55	10.0	10.0	15.0	50.0	50.0	50.0
Cr (μgl^{-1})	0.40 ± 0.59	50.0	50.0	100	50.0	50.0	50.0
Zn (μgl^{-1})	62 ± 42	No guideline	No guideline	No guideline	5000	100	5000

***Secondary Maximum Contaminant level of U.S.A. Secondary Drinking water Standards (non-enforceable)**
USEPA = United States Environmental Protection Agency
WHO =World Health Organization
CCREM = Canadian Council of Resources and Environment Ministers
EEC = European Economic Community (now European Union)
FEPA = Federal Environmental Protection Agency (now Federal Minstry of Environment)

Table 6: Average Values of Physicochemical Characteristics of Water and heavy metals of study area water compared with some guidelines for non-drinking uses of Water

Parameters	Average value of each parameter	Canadian WQGs: Pulp and Paper Industry (Fine Paper) (CCREM, 1987)	Canadian WQGs: Iron & Steel Industry (Manufacture) (CCREM, 1987)	FWPCA 1968 Guideline: Petroleum Industry (Van der Leeden et al., 1990)	Canadian WQGs: Power generating industry (Boiler Feedwate) (CCREM, 1987)	Canadian WQGs: Beverage Industry (Food Canning, Freezedried (CCREM, 1987)	FAO1985G uideline: irrigation water (Limiting conc.) (Van der Leeden et al., 1990)	CSWQCB 1963 Guidelines: Aquatic life protection (freshwater) (Van der Leeden et al., 1990)	Canadian Water Quality guideline: Recreational Water (Water contact limiting) (CCREM, 1987)	FEPA guideline: Textile Industry (Dyeing Process) (FEPA, 1991)	CSWQCB 1963 Gudelines: Livestock Water (Limiting concn.) (Van der Leeden et al., 1990)
Temp. ^{0}C	30.9 ± 1.0	No guideline	<38	No guideline	No guideline	No guideline	No guideline	No guideline	50	No guideline	No guideline
pH at 25^{0}C	6.02 ± 0.09	No guideline	6.8 – 7.0	6.0 – 9.0	8.8 – 9.4	6.8 – 8.5	7.0 – 8.5	6.5 – 8.5	6.0 – 10.0	7.5 – 10.0	5.6 – 9.0
TSS (mgl^{-1})	6.6 ± 1.7	<10.0	No guideline	<10.0	<0.05	<10.0	No guideline	No guideline	No guideline	<5.00	No guideline
TDS (mgl^{-1})	22.4 ± 5.8	<200	No guideline	<750	<0.5	<500	<1500	No guideline	No guideline	<100	No guideline
DO (mgl^{-1})	2.96 ± 0.90	No guideline	No guideline	No guideline	<0.007	No guideline	No guideline	No guideline	No guideline	7.5 or more	No guideline
BOD$_5$	6.4 ± 2.5	-	-	-	-	-	-	-	-	<1.0	-
COD (mgl^{-1})	80 ± 38	No guideline	No guideline	No guideline	<1.0	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline
O & G (μgl^{-1})	2270 ± 480	-	ND	-	-	-	-	0.00	5000	-	-
TPH (μgl^{-1})	2010 ± 340	-	-	-	-	-	-	0.00	5000	-	-
Ni (μgl^{-1})	1880 ± 630	-	-	-	-	-	200	1100	-	-	1000
Cd (μgl^{-1})	3.0 ± 5.3	-	-	-	-	-	10.0	1160	-	-	50.0
Pb (μgl^{-1})	146 ± 55	-	-	-	-	-	-	1340	-	-	100
Cr (μgl^{-1})	0.40 ± 0.59	-	-	-	-	-	100	-	-	-	1000
Zn (μgl^{-1})	62 ± 42	-	-	-	<10.0	-	2000	100	-	-	25000

ND = Not Detected CSWQCB = California State Water Quality Control Board NS = Not Specified
FWPCA= Federal Water Pollution Control Administration CCREM = Canadian council of Resource and environment Ministers
FAO = Food and Agricultural organization FEPA = Federal environmental Protection Agency (Now Federal Ministry of environment

WQGs, The average COD value (80 + 83mg/L) exceeds guideline value for boiler feed water of the power generating industry (< 1.00 mg/L) of the Canadian WQGs). The average value of O & G (2270 + 480 mg/L) and TPH (2010 + 34 mg/l) exceeded guideline value for Aquatic life protection (freshwater) (ND) of the California State Water Quality Control Board (Van der Leeden et al., 1990). The average concentration of nickel in study area (1880 + 630 μg/L) exceeded guideline values for irrigation water (limiting concentrations) (200 μg/L) of the Food and agricultural Organization WQGs (Van der Leeden et al., 1990), Aquatic life protection (freshwater) (1160 μg/L) of the California State Water Quality Control Board WQGs (Van der Leeden et al., 1990) and livestock water (Limiting concentrations) (1000 μg/l) of the California State Water Quality Control Board WQGs. The average concentration of Pb in study area water (146 + 55 μg/L) exceeded guideline value for livestock rearing water (limiting concentration) (100, μg/L) of the California State Water Quality Control Board WQGs (Van der Leeden et al., 1990). It can be seen that the water is not suitable for all the non drinking uses listed. It should however be cautioned here that apart from that by FEPA, these guidelines are strictly not enforceable in Nigeria, these comparisons were

Table 3: Water Quality Characteristic of some other Rivers compared with Benin River in the present study

River	Major Activities in the Area	Temp ^{0}C	pH	TSS mg/l	TDS mg/l	DO mg/l	BOD_5 mg/l	COD mg/l	O & G µg/l	TPH µg/l	Ni µg/l	Cd µg/l	Pb µg/l	Cr µg/l	Zn µg/l	References
Benin River	Industrial Area/Oil Prospecting	27.6 ± 1.6	5.9 ± 1.1	80 ± 130	3360 ± 7700	4.7 ± 1.0	-	-	-	-	-	-	-	-	-	Courant et al., 1987
New Calabar River	Petroleum Indus. Pet. Prospecting	-	-	-	6.50 – 4010	3.40 – 9.10	0.25 – 4.20	10.0 – 1000	5,000, 000	-	-	-	-	-	-	Odokuma and Okpokwasili, 1997
Ogharefe Stream	Oil Prospecting	31	6.2	100	200	3.56	1.60	-	-	-	172	-	107	-	-	Akporido et al., 2009
Adofi River	Oil Prospecting	26.7 ±0.7	6.36 ± 0.10	141. ± 44	32.3 ± 7.6	-	13.1 ± 1.9	28.2 ± 2.9	8.6 ± 1.4	-	-	79 ± 14	7.7 ± 1.9	-	-	Akporid and Moseri, 2009
Osun River (Ogbore)	Industrial Area	-	-	-	-	-	-	-	-	-	-	ND	100	,-	1790	Asonye et al, 2007
New Calabar River	Petroleum Indus. Pet. Prospecting	-	-	-	-	-	-	-	-	-	-	560	850	50.0	-	Wegwu and Akininwor, 2006
Elechi Creek	Pet. Prospecting	30.3	7.3	-	-	6.27	-	-	-	-	-	<1.00	<1.00	<1.00-2.00	-	Davies et al., 2006
Rhine Bimmen River	Industrial area	-	-	-	-	-	-	-	-	-	-	0.70	10.0	11.0	-	Van Der Leeden et al., 1990
Ponggion River Estuary	-	-	-	-	-	-	-	-	-	0.35-1100	-	-	-	-	-	Nayar et al., 2004
Benin River	Industrial Area	30.9 ± 1.0 (29 – 33)	6.02 ± 0.9 (5.77 – 6.20	6.6 ± 1.7 (3.34 – 10.3)	22.4 ± 5.8 (13.3 – 32.0)	2.96 ± 0.90 (1.63 – 5.16)	6.4 ± 2.5 (1.57 - 10.5)	80 ± 38 (15.9 – 132)	2270 ± 480 (1460 – 3230)	2010 ± 340 (1390 – 275)	1880 ± 630 (980 – 3370	3.0 ± 5.3 (0 – 15)	146 ± 55 (35 – 225)	0.40 ± 0.59 (0.00 – 2.00)	62 ± 42 (8.00 – 160)	Present study

made to assess the quality of the water of the present study. The water of the study area was classified into group IV (Prati et al., 1971). Using BOD indices, the water of the study area falls into BOD indices 4 – 8 (i.e. group IV) which means that the water is polluted the water need to be rigorously treated before being used for drinking purpose. A Pearson (2-tailed) correlation of the concentrations of parameters in the study shows that the following pairs correlated strongly and their correlation coefficient are significant at 0.01 confidence level BOD_5 and TDS (correlation coefficient = 0.529), BOD_5 and DO (correlation coefficient = 0.415), TPH and O&G (correlation coefficient = 0.855), Cd and COD (correlation coefficient = 0.410), Zn and TDS (correlation coefficient = 0.410), Zn and BOD_5 (correlation coefficient = 0.441) and Zn and O&G (correlation coefficient = 0.627). Also Zn and TPH (correlation coefficient = 0.333) correlated strongly and the correlation coefficient is significant at 0.05 confidence level. Members of these pairs are either interdependent on each other (e.g. O&G and TPH) or they have identical source. Zn and TPH must have entered the river from the effluents of the lubricating oil factory. A comparison of the results obtained in similar studies elsewhere with the results for the present study are given in Table 5. It is observed that most of the results obtained for the study area were comparable with results obtained for other rivers elsewhere. Some of the results were however higher or lower than these other results. The average COD value for Benin River in the present study (80 ±38 mgl^{-1}) or the range (15.9 – 132 mgl^{-1}) is comparable with those obtained for New Calabar River (10.0 – 1000 mgl^{-1}) and Adofi River (28.2 ± 2.9 mgl^{-1}). The average value of oil and grease obtained for Benin river in the present study (2,270±480 μgl^{-1}) or the range 1460 - 3230 μgl^{-1}) is lower than the average value obtained for New Calabar River (5,000,000 μgl^{-1}). The average concentration of TPH of Benin River in the present study (2010±340 μgl^{-1}) or the range (1390 – 2750 μgl^{-1}) is comparable with that obtained for Pougsion River Estuary (0.38 – 1100 μgl^{-1}). The average value of Ni obtained for Benin River in the present study (1880 ±630 μgl^{-1}) or the range (980 – 3370 μgl^{-1}) is much higher than that obtained for Ogharefe Stream (172 μgl^{-1}). Also the average concentration of Pb obtained for Benin River in the present study (146±55 μgl^{-1}) or the range (35 – 225 μgl-1) is comparable with those obtained for Ogharefe Stream (107 μgl^{-1}) and Osun River (100 μgl^{-1}), It is higher than that for Adofi River (7.7±1.9 μgl^{-1}), and Elechi Creek (<1.00 μgl^{-1}).It is lower than that for New Calabar River (850 μgl^{-1}).

Conclusion

The results obtained in the study indicate that the water is polluted with respect to its use as potable water. The concentration of Ni and Pb are higher than guideline values, the average pH falls lower than pH range of some of the guidelines for drinking water and guidelines for some non-drinking uses of water (i.e. higher acidity).The average concentration of oil and grease and TPH obtained for the study area are also very high (higher than some guideline values) and this also indicate that pollution may have its source in the Lube oil producing factory situated in that area. Water was classified as group IV (Prati et al., 1971, which means the water is polluted with respect to its use for drinking. The presence of high concentrations of the toxic metals (Ni and Pb) and the oil variables (O&G and TPH) has grave consequences for the health of humans and higher animals in the area. Fishing and collection of other animal resources is one of the important occupation of the people in this area. Crop farming is another important occupation. These pollutants can easily enter into the food chain involving himans and higher animals by being available for plant uptake and ingestion by smaller fishes and animal dwelling the river. The presence of these pollutants in the food chain will result in adverse effect on the health of humans and higher animals. It has been observed in this study that this pollutants get to the river through the the effluents from the lubricating oil producing factory. This bad situation can be curtailed by making sure the factory treats its effluent before disposal into the River. Effluent limitation guidelines have been established by relevant governmental Agencies i.e.: Environmental Guideline and standard for the Petroleum Industry in Nigeria by Department of Petrleum Resources in Nigeria (DPR) and National Guidelines and Standards by Federal ministry of Environment (FMEnv.) (Formerly known as Federal environmental Protection Agency). It is however observed that there are lapses in the monitoring of the various industries for compliance with the established guidelines. The Federal Government of Nigeria should ensure that the various industries are properly monitored for compliance with the established guidelines to achieve a healthier environment

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